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Microwave pyrolysis of wheat straw: Product distribution and generation mechanism

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HIGHLIGHTS

- Products data on-line analysis.
- Formation pathways of pyrolysis products and pyrolysis mechanisms.
- The heat and mass transfer during microwave heating process has been investigated.

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ABSTRACT

Microwave pyrolysis of wheat straw is studied, combined with analysis of products, the distribution and generation pathway of products are investigated. Only a small amount of volatiles released when microwave pyrolysis of pure straw. Mixtures of adding CuO and Fe_3O_4 can pyrolyze, and the majority in pyrolysis products is in liquid-phase. Severe pyrolysis occur after adding carbon residue, the CO content in pyrolysis gas products is high, and the maximum volume content of H_2 can exceed 35 vol.%. The high-temperature is helpful for increasing the yield of combustible gas in gaseous products, in particular the H_2 production, but also helpful for improving the conversion of sample. Pyrolysis is carried out layer by layer from the inside to outside. As the internal material firstly pyrolyze and pyrolysis products released pass through the low temperature zone, the chance of occurrence of secondary reactions is reduced.

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1. Introduction

Pyrolysis is one of the most promising thermo-chemical conversion routes for recovering energy from biomass. For obtaining more valuable products and convenient for operation, present researches on pyrolysis are focusing on improving pyrolysis conditions and achieving directional transformation to the targeted-products by adding catalysts and/or adopting new heating methods such as plasma heating, microwave heating and so forth (Huang and Tang, 2008; Tu et al., 2009).

Microwave heating has merits of “internal heating” and the large-sized sample can be heated to reduce the pretreatment processes of raw material for improving the economics of pyrolysis. Consequently, research activities on microwave pyrolysis have been carried out by more and more researchers, including pyrolysis of coffee hulls (Domínguez et al., 2007a), wood (Miura et al., 2004; Santaniello et al., 2012), biomass (Fernández and Menéndez, 2011), waste tea (Yagmur et al., 2008b), corn stover (Lei et al., 2009), wheat straw (Budarin et al., 2009), rice straw (Huang et al., 2008, 2010) and oil palm biomass (Salema and Ani, 2011).

The distribution and composition of pyrolytic products can help in understanding microwave pyrolysis mechanisms of biomass. This is particularly true when these are investigated through on-line analysis (Fu et al., 2010; Ibarra and Moliner, 1991; Li et al., 2001). This paper focuses on microwave pyrolysis of wheat straw under different operating conditions, combined with product analysis, to explore the formation pathways of pyrolysis products and pyrolysis mechanisms under microwave heating.

A variety of additives, including alkali metal carbonates, transition metal oxides, and pyrolytic carbon residue, were used in experiments. The choice of five kinds of additives was based on results of previous studies (Domínguez et al., 2007a; Monsef-Mirzai et al., 1995; Yagmur et al., 2008a; Yang et al., 2006). In this experiment, the average particle size of additives was less than 0.1 mm. The sample (15 g) was pre-mixed with additives, and the mass ratios of additive to biomass were 5, 10, and 20 wt.%.

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2. Methods

2.1. Materials

The biomass used in this study was wheat straw, collected from Liangshan County, Shandong Province in Eastern China. The wheat straw was naturally air dried under sunlight for 30 days to get rid of the surface water. Then it was shredded, grinded and sieved to 0–200 mesh (0–0.090 mm) in preparation for the sample. The proximate and ultimate analysis of the wheat straw sample are carried out (Vario Micro cube EL III, Elementar, Germany), and the results are listed in Table 1. The composition of minerals in biomass ash are listed in Supplementary Table 1. The chemical structures of wheat straw were also identified by Fourier transform infrared spectrometer (Tensor 27, Bruker, Germany) before the experiments (Supplementary Fig. 1).

2.2. Experimental apparatus

Microwave reactor employed in the present study is made by Sanle Microwave Technology Co., Ltd., and has an ability to alter the power intensity in the range of 0–3000 W at a frequency of 2.45 GHz. Metal objects, including wires, cannot normally be placed in a microwave field without either severely distorting it or causing electrical discharges. However, in confirmation of the findings of Menéndez (Menéndez et al., 1999) and Liu (Liu et al., 2004), it is possible to use thermocouples in a microwave oven provided they are thin, have a grounded metal sheath, and are held exactly at 90° to the electric field component of the microwave energy. In the present study, 1 mm-diameter, stainless steel sheathed type K (chrome-alumel) thermocouples are used, covering the temperature range of 0–1000 °C. More details of this MWR can be found in our previous study (Zhao et al., 2012).

2.3. Experimental procedure

The sample was weighed and placed in a special quartz vessel, and then the tetrafluoroethylene flange was installed and the vessel was sealed. Carrier gas (99.99% N_2) was introduced into the reaction vessel from the lower portion and the flow rate was 3 L/min to keep the inert circumstance. The cumulative flow meter was fixed at the outlet of the reaction vessel. At the end of experiments, the value of cumulative flow meter minus the total cumulative flow of nitrogen was the total volume of product gases.

After opening the microwave, the sample was heated and pyrolyzed. The volatiles released with the carrier gas were introduced into a condenser (mixture of ice water), then the condensable gas condensed in the condenser, and the non-condensable gases through glass were introduced into FTIR analyzer for on-line analysis after removing the dusts with wool and drying with silica. The products flowed out the gas line were collected with a bag for further GC analysis. After pyrolysis, the pyrolysis residue was removed and weighed to determine the yields of solid products after pyrolysis process. The carrier gas kept purging until the solid residue (coke) was self-cooled to below 100 °C.

The yield of product gases was the cumulative production of various products released during the pyrolysis process, and the specific method was: the yield of each gas, such as CO_2, CO, CH_4, and many other light hydrocarbons, was obtained by the concentration measured by Fourier transform infrared spectrum gas analyzer plus the total volume (gas products volume and carrier gas volume); the total volume of gas products was obtained by the value of accumulated flow meter subtracting the total volume of carrier gas, and then through the subtracting method, the volume of H_2 was obtained. Then the mass production of the product gases can be obtained conversion at ambient, this method was widely used in many studies (Yagmur et al., 2008a; Yang et al., 2006; Chen et al., 2003). The yield of liquid products was obtained by subtraction, including tar, water-soluble organic matter, water and some small coke particles.

Table 1
Ultimate and proximate analyses of samples.

M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C_{ad}	H_{ad}	N_{ad}	S_{ad}	O[a]
7.40	5.90	69.30	17.40	41.41	5.86	1.44	0.17	45.22

[a] Subtraction.

2.4. Analysis of products

The composition of the gas products was analyzed by an Agilent 6890N gas chromatography/dual thermal conductivity detector with a GDX401 capillary column and 5A molecular sieve. The temperature of the injector, oven, and detector was 100, 80, and 150 °C, respectively. The flow rate of the carrier gas was 15 ml/min without splitting.

To determine the main composition of the gas products, online FTIR analysis of the gas products was carried out. The condensed and dried gases were directly introduced into the FTIR analyzer (DX4000, GASMET, Finland). The carrier gas flow was 3 L/min, designed to make gas products as fast as possible at a lower temperature and reduce the occurrence probability of the secondary decomposition of the primary products. The temperature in the test chamber and the gas transmission pipeline was kept at 180 °C to prevent the condensation and absorption of the semi-volatile gas products. The volume flow of gas products was determined with a flow meter at the outlet of the FTIR analyzer. Then the weight of gaseous products was obtained by the total volume multiplied by the average molecular weight and the weight of liquid products was obtained by subtraction of gas products and solid products from the total weight of sample.

The solid products were ground to fine particles using a mortar and subjected to FTIR spectrometer (Tensor 27, Bruker, Germany). The IR spectra were between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}. The surface property of coke (i.e., surface area, pore distribution, and volume) was analyzed using an acceleration pore surface area porosimetry instrument (ASAP 2020, Micromeritics, USA), with liquid nitrogen as the adsorbent in the adsorption isotherm under 77 K. Multi-point Brunauer, Emmett, and Teller (BET) surface area analysis method was used. V_T is the total pore volume, and the average pore diameter $d_{ave} = 4V_T/S_{BET}$.

3. Results and discussion

3.1. Effect of microwave power on pyrolysis

Previous researches have shown that the heating rate and the final pyrolysis temperature are key impacting factors for that affect pyrolysis processes and product characteristics (Guo et al., 2013; Fu et al., 2012; Angın, 2013). The heating rate and the final pyrolysis temperature of the sample are mainly influenced by microwave power. The higher the microwave power, the greater the heat generated inside the sample, and the faster the increase in temperature. It has been also confirmed that the higher the microwave power, the higher the temperature of final pyrolysis (Huang et al., 2013). Therefore, this section mainly focuses on the impacts of microwave power on product distribution and composition for microwave pyrolysis of pure straw.

3.1.1. Distribution of pyrolysis products

The pyrolysis product distribution of wheat straw at different microwave powers is shown in Supplementary Fig. 2. The heating rate during the heating process was low due to the limited ability of pure straw to absorb microwaves; the final pyrolysis temperature was also not too high. Throughout the process, drying/torrefaction of straw occurred. In addition, because the temperature inside the sample was relatively high, a small amount of volatiles released from the composition easily decomposed contained in internal sample (Huang et al., 2008). The general trend observed was that with increasing microwave power, the sample conversion rate increased, the amount of solid residue decreased, and the amount of gas and liquid products increased.

The weight loss of pure straw under different microwave power was very small. Even at a microwave power of 800 W, the residual solids is still more than 70 wt.%, indicating that complete pyrolysis did not occur. The reasons are as follows. In investigating the weight loss and heating characteristics of wheat straw, an open reaction vessel was used, and the protective atmosphere (N_2) was passed directly into the furnace, which is conducive to the release of moisture and volatile products. However, when collecting product gases for analysis, the reaction vessel and piping need to be connected and sealed. Thus, water evaporated during heating, and the aqueous products released during pre-pyrolysis could easily condense onto the cooler walls of the reaction vessel and connecting pipeline, which also absorb a large amount of microwaves, resulting in slow heating of the sample, and in its difficulty to pyrolyze. Only through increasing the protective gas flow and extracting water from the reaction vessel in time, can the sample continue to heat up and undergo pyrolysis. However, increasing the protecting gas flow and using sealed containers would increase heat loss and pressure inside the container, which is not conducive to the release of gaseous products, increasing the difficulty of the reaction, and eventually not leading to dramatic weight loss, even at a high microwave power.

3.1.2. Analysis of product characteristics

The conversion ratio of the sample was low due to incomplete pyrolysis, and almost no liquid products were collected. Thus, the solid and liquid products were not analyzed.

The volume content of each gas composition in product gases were shown in Table 2.

Table 2
Gas product analysis of microwave pyrolysis of pure straw.

Microwave power/W	CO_2/vol.%	CO/vol.%	CH_4/vol.%	C_{2+}/vol.%	H_2/vol.%
400	54.27	25.83	0.17	1.9	17.83
600	54.02	23.98	0.24	0.67	21.09
800	42.99	25.48	0.24	1.83	29.47

The volume contents of CO_2 and CO in gas products obtained by microwave pyrolysis of pure straw are very high, for reasons closely related to the formation mechanisms of CO_2 and CO. Numerous studies show that the generation temperature of CO_2 and CO is low, with these primarily formed by extrusion of carbonyl groups and carboxyl groups (Ferdous et al., 2001). Through functional group analysis, it was noted that a large number of functional groups (such as carbonyl groups) were contained in the sample, resulting in large amounts of CO_2 and CO in pyrolysis products. In addition, the volume content of CO_2 decreased with increase in microwave power. This is because with the increase in microwave power, the pyrolysis of the internal sample deepened, and more and more other gases (i.e., not CO_2), primarily H_2, were formed. The volume contents of CH_4 and light hydrocarbons were very low. The reason is that CH_4 and light hydrocarbons are mainly formed by cracking of hydrocarbon molecules, and only a small amount of CH_4 formed by methyl is released from biomass (Dufour et al., 2009). For obvious reasons, the experimental conditions in this case were not conducive to their formation.

Based on comprehensive analysis of product distribution and gas products, the following conclusions were obtained. When using pure straw as the experimental sample, lower conversion ratio and total gaseous products were obtained. CO_2 content in the product gas was close to 50 vol.%, but was difficult to use.

The trends of gas component concentration in product gas over time under different microwave powers are shown in Fig. 1. The gas component concentration of each gas component is the concentration of total gas, including protective gas.

With increase in microwave power, the release peak of the gas was advanced, and the peak concentration was also significantly increased, consistent with the finding that the higher the microwave power, the faster the temperature rise and the temperature achieved. The concentration of CO_2 increased with increase in microwave power, but because of the larger volume growth of H_2, the percentage of CO_2 in the total gas output decreased.

3.2. Effect of additives on the pyrolysis process

Due to the poor absorption of microwaves by straw, the temperature increased slowly during microwave heating, or no pyrolysis occurred. Addition of suitable additives can decrease the activation energy of pyrolysis, increase the heating rate of the sample, and improve the final pyrolysis temperature, thereby improving the microwave pyrolysis process. This section mainly investigates the influence of adding different types and proportions of additives on the pyrolysis process and on product distribution.

3.2.1. Product distribution

The product distribution at microwave power 800 W and add different kinds and proportions of additives are listed in Table 3,

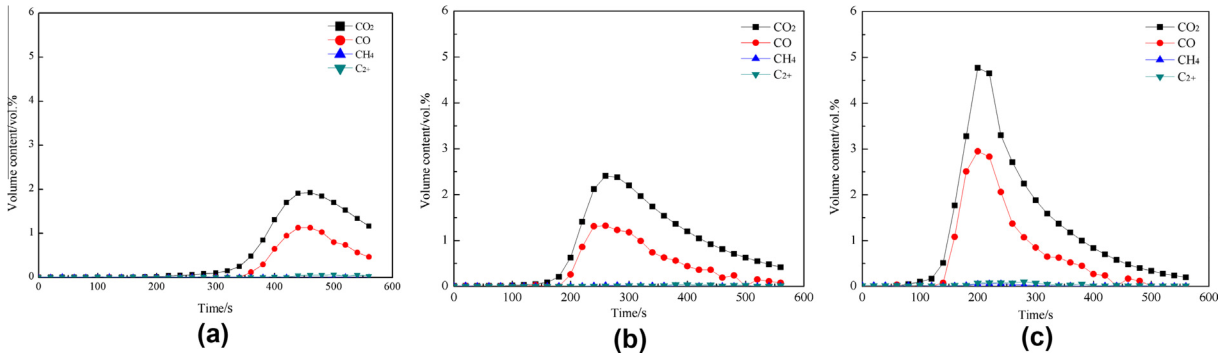

Fig. 1. The trends of gas composition under different microwave powers (a-400 W, b-600 W, c-800 W).

Table 3
Product distribution on different additives and adding ration under microwave power 800 W.

Adding ratio	Additive	Gas/wt.%	Liquid/wt.%	Solid/wt.%
5 wt.%	Pyrolytic residue	44.11	27.45	33.44
	K_2CO_3	22.64	49.86	27.50
	Na_2CO_3	22.16	50.41	27.43
10 wt.%	Pyrolytic residue	46.55	26.08	27.36
	CuO	7.93	21.21	70.86
	Fe_3O_4	7.95	22.84	69.21
	K_2CO_3	24.40	48.73	26.87
	Na_2CO_3	26.10	48.09	25.81
20 wt.%	Pyrolytic residue	60.94	13.67	25.39
	CuO	21.16	52.92	25.92
	Fe_3O_4	21.70	55.82	22.48
	K_2CO_3	48.95	24.19	26.86
	Na_2CO_3	56.86	20.87	22.27

and the results at microwave power 600, 400 W are listed in Supplementary Tables 2 and 3.

When the microwave power was high enough and a large proportion of additive (20 wt.%) was added, the mixture pyrolyzed with the addition of CuO and Fe_3O_4. The pyrolysis products were mostly in the liquid-phase, and under some conditions, accounted for 50 wt.% or more of the total amount of sample. CuO and Fe_3O_4 are evidently inappropriate as absorbents for the purpose of obtaining gas products; however, for obtaining liquid products, these can be considered.

Alkali metal salts can promote the formation of gas products, but only with the adding proportion being 20 wt.% and with higher temperatures (microwave power) can this effect be fully demonstrated. This is because alkali metal salts can promote the condensation reaction of high molecular components at high temperatures, generating small molecules of gaseous products and coke, and thereby reducing the yield of bio-oil and producing more coke and gas products. As can be seen in Table 3, when the adding ratio was less than 20 wt.%, although a higher conversion rate of the sample was achieved, the main products derived were in liquid form, and a smaller proportion of gaseous products (about 20 wt.%) was obtained.

As long as the adding ratio of pyrolytic carbon residue is high enough, it is sufficient to trigger pyrolysis, and the yield of gas products is the highest, except for very few exceptions. This finding illustrates an important relationship with fast heating and high temperatures achieved.

The product distribution after adding 10 wt.% of different types of additives under microwave power 800 W is shown in Supplementary Fig. 3. The conversion rate was high after adding pyrolytic carbon residue, getting close to 50 wt.% of gas products. When CuO and Fe_3O_4 were added, incomplete pyrolysis of the sample occurred, and the conversion rate was lower, producing a small amount of gas products. After adding alkali metal salts, a high conversion rate of the sample was achieved, but due to low adding ratio and poor ability to absorb microwaves, the heating process of the mixture was slow, resulting in water and other primary products of pyrolysis gases being removed by the protecting gases. Thus, the high-temperature reaction of water and other primary products with carbon to form non-condensable gases did not occur fully, and less gas products were obtained, with mostly liquid products.

3.2.2. Analysis of products

3.2.2.1. Gas products. The contents of gas product at microwave power 800, 600, 400 W and add different kinds and proportions of additives are listed in Supplementary Tables 4–6.

When, after addition of CuO and Fe_3O_4, strong pyrolysis did not occur, high proportions of CO_2 were contained in the product gas; however, there was a big difference when pyrolysis occurred. In this case, the gas products contained a higher level of H_2 after addition of CuO, while adding Fe_3O_4 resulted in a higher content of CO in gas products, in agreement with existing studies (Dufour et al., 2009). This is because, at high temperatures, a reduction reaction occurs between carbon and Fe_3O_4, and CuO has some catalytic effect on thermal cracking of CH_4.

As long as the adding ratio of pyrolytic carbon residue is high enough, the sample can be dramatically pyrolyzed. In this case, the volume content of CO_2 in gas products was relatively low, while the CO content was generally higher, mainly because the gasification reaction of pyrolysis char with CO_2 occurred at high temperature (Menéndez et al., 2007). The volume content of H_2 was highest at 35 vol.%, at microwave power of 400 W, at which point the volume ratio of CO and H_2 was close to 1:1. In addition, as pyrolytic carbon residue can be used repeatedly and is easy to obtain, carbon residue is the most advantageous additive for preparation of gas products.

Higher volume content of H_2 (generally more than 40 vol.%) was obtained after adding alkali metal carbonate, while the volume contents of CO_2 and CO were relatively low. The volume content of syngas in gaseous products, after addition of pyrolytic carbon residue and carbonate, exceeded 70 vol.%, indicating that, compared to conventional pyrolysis, microwave pyrolysis has an advantage in terms of production of syngas.

The composition analysis of pyrolysis gas products add 10 wt.% additives is shown in Fig. 2.

Seen from Fig. 2, the volume content of CO_2 decreased with an increase in microwave power, because the higher the microwave power, the higher the heating rate of the sample, and the shorter its residence time under low-temperature conditions; this is not conducive to extrusion of CO_2. At high temperatures, CO_2 will react with carbon to generate CO, which may be one of the reasons for reduction in CO_2 content. In addition, it may explain why the yield of CO increases with increase in microwave power. The volume content of CH_4 decreased slightly, while the volume content of H_2 improved, likely caused by secondary reactions of tar and other macromolecules, and thermal cracking of CH_4 at high temperatures.

After addition of K_2CO_3 (Supplementary Fig. 4), the volume content of CO_2 in pyrolysis product gas was high, and the volume

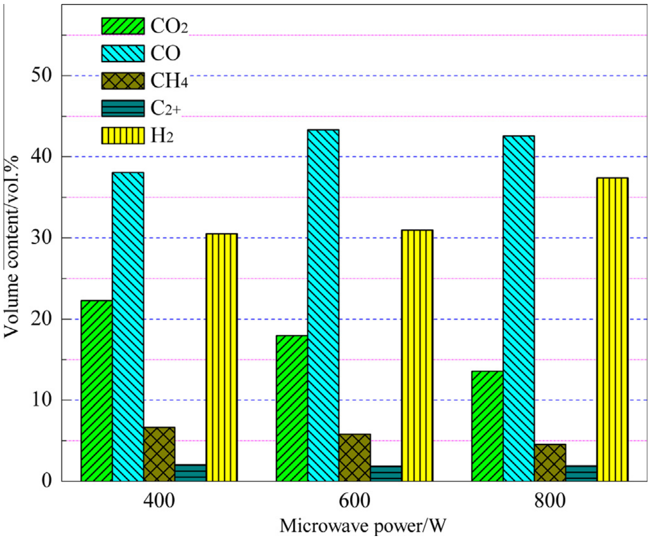

Fig. 2. Gas product contents after adding 10 wt.% of pyrolytic residue under different microwave power.

content of CO was low. This is because the heating rate of the mixture with added K_2CO_3 is far lower than that with added carbon residue, while the final pyrolysis temperature is relatively lower. Thus, the residence time of the sample with added K_2CO_3 in low-temperature conditions was longer, and more CO_2 was released. Conversely, both the lower final pyrolysis temperature and the addition of K_2CO_3 were not conducive to high-temperature gasification of carbon and CO_2. In addition, from the perspective of chemical reaction equilibrium, the facilitating role of carbon residue addition on the gasification reaction between pyrolysis char and CO_2 at high temperatures cannot be ignored.

The volume content of H_2 in gas products obtained after addition of K_2CO_3 should be higher than that obtained from addition of residual carbon (about 10 vol.%, or more). This is because of the catalysis of K_2CO_3 for the secondary cracking reaction of tar and thermal cracking of CH_4 (Demirbas, 2002). The general trend is that with increase in microwave power, the volume content of combustible gas increases, and the volume content of CO_2 continues to decrease.

The volume content of CO_2 in pyrolysis gas decreases rapidly with increase in microwave power after adding 10 wt.% Na_2CO_3 (Supplementary Fig. 5). At microwave power of 600 W, the maximum volume content of CO was achieved, and H_2 content changed little in comparison with that obtained at 400 W. When microwave power was 800 W, the maximum volume content of H_2 was achieved, and CO content decreased, compared to the content at 600 W; however, this was still higher than the volume content obtained at a microwave power of 400 W.

Two gas releasing peaks existed at microwave power of 400 W, which is shown in Fig. 3, verifying the inference that the internal and external samples do not undergo pyrolysis simultaneously. With an increase in microwave power, the temperature gradient between the internal and external sample increases, and the heat transfer process is strengthened, resulting in a smaller time interval between internal and external samples.

3.2.2.2. Solid products. (1) Analysis of surface porosity

The structural properties (surface area, average pore diameter, and pore volume, etc.) of coke obtained are shown in Table 4. As can be seen from the table, most volatiles were released and the maximum specific surface area of the solid products was obtained (about 128.71 m²/g) as a result of the maximum material temperature produced by addition of carbon residue. Addition of alkali metal carbonate promotes the condensation reaction of solid products. Moreover, due to the poor plasticity of coke produced by straw, the specific surface area of solid product is small.

(2) Analysis of functional groups

Based on the IR spectrogram of solid cokes (adding proportion of 10 wt.%), the main functional groups of coke are C–C (1475–1435 cm^{-1}, alkane, R-CH_3, R′–CH_2–R ‘or aromatic ring), CO–(C) (1275 cm^{-1}), CO–(H) (1050 cm^{-1}) and C–H (865–810 cm^{-1}, C_{5+} olefin or aromatic ring). The OH was removed rapidly. Moreover, the IR absorption band of the C–H bond (olefins) decreased quickly; this was attributed to the rupture of weak alkyl C–H bonds, which favor the formation of gaseous hydrocarbons (CH_4, C_2H_6, and C_2H_4). The content of element H in coke decreased markedly. The IR absorption band of O=C=O (CO_2) existed in the sample and the IR absorption band of O=C=O (CO_2) in coke rapidly decreased to zero, due to rapid release of CO_2. The C=O (1700 cm^{-1}) bonds within the samples were easily broken, to form CO and CO_2, as there was no IR absorption band of C=O bonds in solid products.

Table 4
The S_{BET} d_{ave} and pore volume V_T of solid products under different conditions.

Sample	Microwave power/W	S_{BET}/(m^2/g)	V_T/(cm^3/g)	d_{ave}/Å
Pure straw	600	31.96	0.027	33.26
10 wt.% pyrolytic residue	600	128.71	0.094	29.23
10 wt.% K_2CO_3	400	8.09	0.011	52.01
10 wt.% K_2CO_3	600	6.97	0.010	58.78
10 wt.% Na_2CO_3	600	12.69	0.015	47.22
10 wt.% K_2CO_3	800	8.91	0.010	46.28

Table 5
The element analysis of solid products under different conditions(wt.%, *d*).

Sample	C	H	O	N	S
10 wt.% pyrolytic residue	46.85	0.78	45.94	0.53	–
5 wt.% Na_2CO_3	59.85	1.37	31.85	1.02	–
20 wt.% Na_2CO_3	64.63	1.78	26.45	1.24	–
10 wt.% Na_2CO_3	61.79	1.65	29.35	1.32	–
5 wt.% K_2CO_3	61.16	1.45	30.61	0.89	–
10 wt.% K_2CO_3	61.42	1.65	30.07	0.96	–
20 wt.% K_2CO_3	60.85	2.07	30.24	0.95	–

(3) Analysis of elements

C and O were the major elements in solid products, and small amounts of H, N, S, and other elements were also included, listed in Table 5. The content of O and H decreased, because of the removal of the –OH bonds and condensation reactions. After adding pyrolytic carbon residue, the C content was significantly less than the values obtained under other conditions, while the O content increased, reaching 45.94 wt.%. The reason is the CO_2 in product gas reacted with residual carbon to form CO at high temperatures, enhancing the relative amount of oxygen in solid products. Adding different proportions of alkali metal carbonate can promote condensation reactions, and improve the C content in solid products significantly.

3.3. Formation pathways of products and reaction mechanisms

Microwave pyrolysis is a very complex thermal chemical conversion process, and a series of chemical changes and physical changes of the sample occur. The chemical changes comprise a

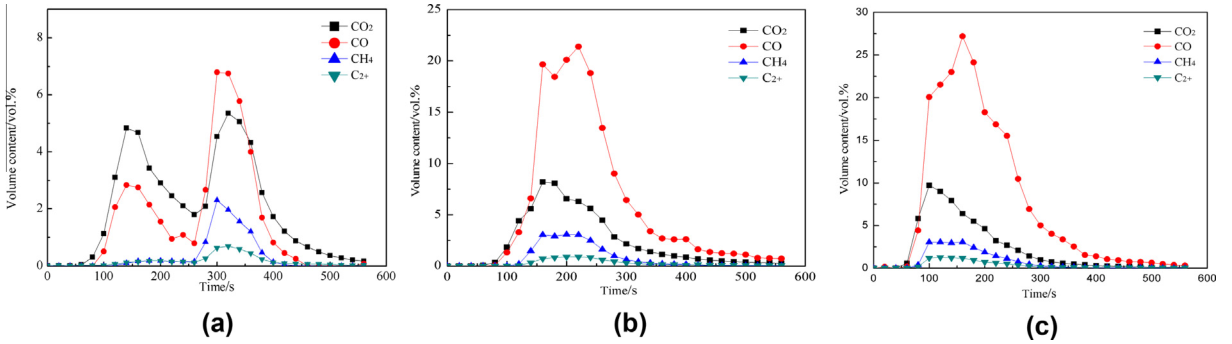

Fig. 3. The trends of gas composition under different microwave power added 10 wt.% pyrolytic carbon residue (a-400 W, b-600 W, c-800 W).

series of complex chemical reactions, and the physical changes comprise energy conversion, heat transfer, and mass transfer. Through study of conventional pyrolysis mechanisms, integrated microwave heating characteristics and pyrolysis characteristics, formation pathways of products and reaction mechanisms of microwave pyrolysis were analyzed, from the following perspectives.

3.3.1. From the composition and functional group analysis

Wheat straw is composed of cellulose (30%), hemicellulose (50%), and a small amount of lignin extract (15%) and ash composition. Compared to the hemicellulose and lignin, cellulose has a simplest structure and has the minimal change in chemical structure. The thermal stability of cellulose is low, and it begin to pyrolyze at the temperature of 325 °C. When pyrolysis occurs, the molecular structure of cellulose is destroyed, and the degree of polymerization decreased. Reactions occurred during pyrolysis include depolymerization, hydrolysis, oxidation, dehydration and other decarbonylation reactions (Yang et al., 2007).

Hemicellulose has a large difference with cellulose, manifested in that not only the content in plant species is different, but the structure is different. The presence of branches not only increases the complexity of the structure of hemicellulose, but also affects the properties of hemicellulose. In fact, hemicellulose is a variety of sugars copolymers in general. The branches are unstable and easily to hydrolysis or pyrolysis under the influence of external factors, usually starts near 200 °C. Also, its decomposition temperature was narrowest, and in the initial stage of decomposition of cellulose and lignin, the majority of hemicellulose has pyrolyzed completely. Compared to pyrolysis of cellulose, the pyrolysis of hemicellulose generates more gas products, and less liquid product.

The structure of lignin is complicated and has a kind of aromatic character. Lignin and cellulose are often banded, calling lignocellulose. A variety of chemical bonds are broken during the lignin pyrolysis process, including the C–O band in methoxy groups, the C–O band in phenoxy groups and the C–C bond in propyl groups. The cleavage of these bonds will form a large and lively benzene-containing radical, which are easily react with other molecules or radicals for condensation reaction and more stable macromolecular structure are formed, and thus coking.

From the view point of functional groups, the main chemical compositions of wheat straw are oxygen-containing functional groups, such as alkyl, ether, aromatic, ketone, alcohol. Due to the highly reactive and low activation energy characteristics, pyrolysis of oxygen-containing functional groups is easier at low temperature, forming a large number of CO and CO_2 (Demirbas, 2000). CO_2 is considered to be the products of low temperature carbonization of biomass, and slow release of CO is caused by molecule reforming and isomerization of some volatiles with a hydroxyl group or a carbonyl group at the high temperature section. The bond energy of functional group methoxy is lower, and at a low temperature it can be cracked and reformed, releasing CH_4. And rupture of methylene groups in volatiles at the high temperature increases the CH_4 production. H_2 is mainly produced by the opening and reforming reaction of aromatic rings at the high temperature, and with the increase of pyrolysis temperature, the secondary cracking of volatiles released more H_2. Hydrocarbons such as C_2H_6 and C_2H_4 are mainly produced from the secondary cracking of volatile matters, and the yields are relatively few, and the release temperature is relatively high.

3.3.2. Analysis of the transfer of mass and energy

Microwaves have the characteristic of "penetrating," and will continuously decay during the propagation process of penetrating the material, being converted into heat, and causing a rapid increase in temperature of the material. Assuming no heat loss on the particle surface, the surface temperature of the material should be highest and decreases gradually from outside to inside, with the same tendency as microwave distribution.

The reality is, however, that because microwave heating has the characteristic of "selective heating," there is a big temperature difference between the container and material, resulting in heat loss from the material surface being very large. Although the microwave energy absorbed by internal materials is relatively small, heat accumulates inside the internal material, as the thermal conductivity of biomass material is usually small and the heat transfer process of the inner layer to the outer material is very slow. Thus, when using microwave heating, the temperature of the internal material is often higher than the temperature of the external sample. The entire process reflects the combined effects of microwave transmission and transformation, heat and mass transfer, and chemical reaction (pyrolysis), which is a very complex process.

Fig. 4 is a schematic diagram of energy conversion and heat and mass transfer processes in an ideal case. The ideally means: the material size is not too small to cause pyrolysis of the internal sample, while also not being too large to cause no pyrolysis of the center sample. Pyrolysis of a layer of intermediate material occurs, called the "annular reaction zone".

The microwave pyrolysis process of the sample can be described as follows. Microwaves penetrate the sample and continue to decay, and the microwave energy is transformed into heat. Due to the heat loss effects of the surface, heat constantly accumulates inside the material and is transferred outwards. This is demonstrated by the fact that the internal temperature of the sample is high, while the external temperature is low.

Pyrolysis occurs layer by layer from inside to outside. Parts of the biomass particles are heated rapidly and decompose into carbon and volatiles. Due to the fact that pyrolysis of the internal material occurs first, the primary pyrolysis products released will pass through a low temperature zone, and the probability of occurrence of secondary cracking thus drops significantly. With heat transfer, the external particles are heated and pyrolyzed again, and most of the volatiles released in the process are diffused to the low temperature area outside, while only a few are diffused to the internal high temperature zone.

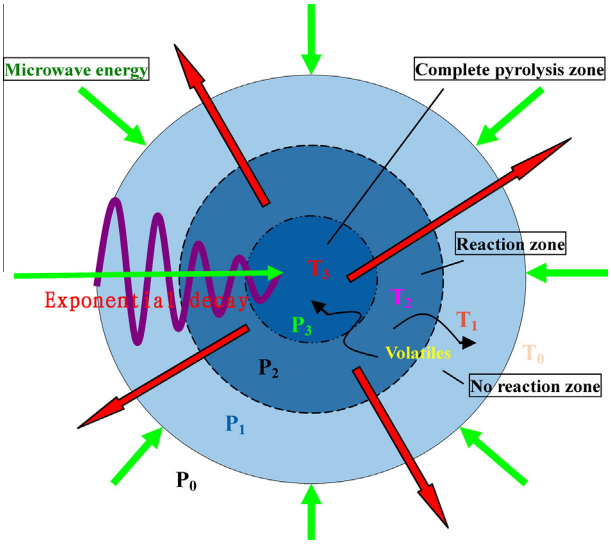

Fig. 4. Schematic diagram of energy conversion and heat and mass transfer process during microwave heating (T – Temperature, $T_3 > T_2 > T_1 > T_0$; P – Press, $P_3 > P_2 > P_1 > P_0$).

The strong microwave absorption capacity of water must be considered. In the microwave heating process, the water contained in the material will evaporate quickly. This means that the probability of a conversion reaction with the high-temperature carbonized layer and gas products such as CH_4 and CO is low. However, in the conventional pyrolysis process, the drying process and the release process of volatiles occur almost simultaneously; and thus, the probability of water in the conversion reaction is larger.

3.3.3. Analysis of secondary reactions

When the sample's temperature is high, secondary cracking reactions of pyrolysis gases occur, and more permanent gases (CO, CO_2, and H_2, etc.) are formed. This results in a rapid increase in gas production. The main reactions involved in secondary pyrolysis are shown in equations (Dai et al., 2000).

$$\mathrm{Tar(g)} \rightarrow \mathrm{CH_4(g)} + \mathrm{H_2O(g)} + \mathrm{CmHn(g)} + \mathrm{H_2(g)} \tag{4-2}$$

$$\mathrm{CH_4(g)} + \mathrm{H_2O(g)} \leftrightarrow \mathrm{CO(g)} + 3\mathrm{H_2(g)}, \quad \Delta H_{298\mathrm{K}} = 206.1\ \mathrm{kJ/mol} \tag{4-3}$$

$$\mathrm{C(s)} + \mathrm{H_2O(g)} \leftrightarrow \mathrm{CO(g)} + \mathrm{H_2(g)}, \quad \Delta H_{298\mathrm{K}} = 132\ \mathrm{kJ/mol} \tag{4-4}$$

$$\mathrm{CO(g)} + \mathrm{H_2O(g)} \leftrightarrow \mathrm{CO_2(g)} + \mathrm{H_2(g)}, \quad \Delta H_{298\mathrm{K}} = -41.5\ \mathrm{kJ/mol} \tag{4-5}$$

$$\mathrm{C(s)} + \mathrm{CO_2(g)} \leftrightarrow 2\mathrm{CO(g)}, \Delta H_{298\mathrm{K}} = 173\ \mathrm{kJ/mol} \tag{4-6}$$

$$\mathrm{CH_4(g)} \leftrightarrow \mathrm{C(s)} + 2\mathrm{H_2(g)}, \quad \Delta H_{298\mathrm{K}} = 75.6\ \mathrm{kJ/mol} \tag{4-7}$$

$$\mathrm{CH_4(g)} + \mathrm{CO_2(g)} \leftrightarrow 2\mathrm{CO(g)} + 2\mathrm{H_2(g)}, \quad \Delta H_{298\mathrm{K}} = 260.5\ \mathrm{kJ/mol} \tag{4-8}$$

$$\mathrm{CmHn(g)} + 2n\mathrm{H_2O(g)} \rightarrow n\mathrm{CO_2(g)} + [2n + (m/2)]\mathrm{H_2(g)} \tag{4-9}$$

$$\mathrm{CmHn(g)} + n\mathrm{H_2O(g)} \rightarrow n\mathrm{CO(g)} + [n + (m/2)]\mathrm{H_2(g)} \tag{4-10}$$

Generally, these Eqs. (4-4), (4-5), (4-9), (4-10) are considered to be the main secondary cracking reactions in conventional pyrolysis, and Eq. (4-6) can be ignored because of the requirement for higher reaction temperature (>800 °C). In the microwave pyrolysis process, however, due to the special nature of microwave heating, the secondary cracking pathway of volatiles is markedly different from that of conventional pyrolysis. In addition, reactions involving H_2O are weakened as a result of release of water.

The changing trend of H_2 can be used to characterize the degree of secondary pyrolysis – the higher the production of H_2, the more thorough the secondary pyrolysis process is (Dai et al., 2000). It can be concluded that H_2 production increases rapidly with increase in temperature – high temperatures are conducive to the occurrence of secondary reactions. The increase in H_2 production can be explained by the thermal cracking of tar and fixed carbon conversion, but the higher level of CO in microwave pyrolysis cannot be explained satisfactorily.

3.3.4. Analysis of effects of catalysts and "hotspots"

When the sample was heated by microwaves and pyrolysis occurred, the "bright spot" could be clearly observed, especially at the intense pyrolysis stage. This suggests that the formation of "microwave plasma", which is likely related to metal minerals (Menéndez et al., 2007). Materials which have a strong ability to absorb microwaves, such as Fe_3O_4, CuO, and pyrolytic carbon residue, were added to the sample, whose temperature was much higher than the biomass particles, and the biomass particles were heated by heat transfer. The temperature of "microwave plasma" or microwave absorbent particles should be substantially higher than that of the measured thermocouple. Under such circumstances, it is expected that at a lower temperature or at the initial stages of the pyrolysis process, reactions between high temperature carbon particles, CO_2, and H_2O (the Eqs. (4-4) and (4-6)) will be promoted. Thus, compared with conventional pyrolysis, gas products obtained through microwave-assisted pyrolysis are richer in H_2 and CO, and the CO_2 content is lower.

In addition, metal salts contained in the ash also have a significant effect on pyrolysis. Potassium will promote Eqs. (4-6) and (4-8), because it will act as a catalyst and prevent the deposition of coke on the catalyst. In addition, high temperatures will promote balance in the direction of generating CO. C, Fe, and alkaline oxides can promote hydrocarbon cracking and dry reforming reaction of methane (reaction 4-7, 4-8). Ni can promote cracking of methane, and K and Na will catalyze the gasification reactions of C and CO_2. Ca, Cu, Fe, and Zn will promote the water gas shift reaction (Domínguez et al., 2007b).

3.4. Energy balance analysis of system

The energy required for the reactions, the enthalpy of the products, and the heat losses of the system should be determined, in order to calculate energy utilization efficiency of the entire system. The energy balance of the whole system can thus be expressed as (Ding and Jiang, 2013):

$$Q_{input}\Delta t = Q_{losses-conversion}\Delta t + Q_{thermal-losses}\Delta t + Q_{losses-reflection}\Delta t + m_1\Delta H_{reaction} + m_2\Delta H_{production} \tag{4-11}$$

Q_{input} – input power of system, W;

$Q_{losses-conversion}$ – conversion losses in circuit and magnetron, W;

$Q_{thermal-losses}$ – heat losses in radiation, convection forms, W;

$Q_{losses-reflection}$ – energy absorbed by water load, W;

$\Delta H_{reaction}$ – reaction endothermic, J/kg;

$\Delta H_{production}$ – product enthalpy, J/kg;

m_1 – mass of reactants, kg;

m_2 – mass of products, kg;

Δt – reaction time, s.

The energy balance of the entire experimental system shown in Fig. 5 was calculated using the following experimental conditions: microwave power 400 W, pyrolysis temperature 600 °C. Power supply into the system is: Q_{input} = 4000 V ×

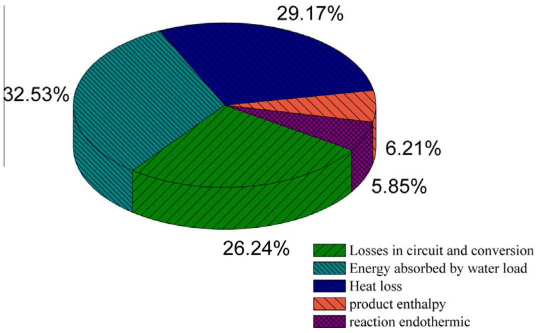

Fig. 5. Energy balance analysis of microwave pyrolysis system.

0.135 A = 540 W. The microwave power is set as the output value, and thus reflects the circuit and conversion loss: $Q_{losses-conversion}$ = 540 W − 400 W = 140 W.

The power of the products is 33.15 W, calculated based on their temperature and enthalpy. The power consumed by the reaction was determined to be 31.2 W. The microwave energy reflected and absorbed by water was 180 W, calculated using the flow and the temperature difference in water flow out of the circulator. Calculation of heat loss is very complicated; and therefore, this was calculated by subtraction, giving the value of 155.65 W.

Because of the small amount of material, and its poor capability to absorb microwaves, most of the energy was reflected to the waveguide. The energy losses in transformers and magnetron accounted for about 26%, and the power loss caused by the heat loss was about 29%. The heat loss of the reaction system was quite high, probably due to the following two reasons: (1). Small size of the device––the ratio of surface area to the volume of the reactor was too high, increasing the heat loss; (2). Microwave heating has the characteristic of "selective heating." The ambient temperature is relatively low, increasing radiation and convection heat losses. However, when the system is enlarged to the industrial application scale, the ratio of energy for pyrolysis reactions to total energy should be increased significantly. In addition, improving the conversion efficiency of electricity to microwave energy is necessary for industrial application of the apparatus.

4. Conclusions

Only drying occurs during microwave heating process of pure straw. At a high proportion and the microwave power is high enough, mixtures of adding CuO and Fe_3O_4 can pyrolyze; the majority in pyrolysis products is in liquid-phase. After adding carbon residue, the volume content of CO_2 in pyrolysis gas products is low, the CO content is high, and the maximum volume content of H_2 can exceed 35 vol.%; Pyrolysis is carried out layer by layer from the inside to outside, and the chance of occurrence of secondary reactions during microwave pyrolysis is reduced as the special heat transfer.

The FTIR spectra of solid coke under different pyrolysis conditions (added ration 10 wt.%) is shown in Supplementary Fig. 6.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.01.094.

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